

# PATENT SPECIFICATION

NO DRAWINGS

1034.526

1034.526



Date of Application and filing Complete Specification April 22, 1963.

No. 15810/63.

Application made in United States of America (No. 191759) on May 2, 1962.

Complete Specification Published June 29, 1966.

© Crown Copyright 1966.

Index at acceptance: —B2 E(1A, 1H); B5 N(2F, 2G, 2N3, 2X, 10B3, 12, 13, 14, 16B3); H5 H2E4B

Int. Cl.: —B 31 d//B 32 b, H 05 b

## COMPLETE SPECIFICATION

### Improvements in Electrically Conductive Stable Coating

We, CHEMELEX, INC., a corporation organized and existing under the laws of the State of New York, United States of America, of 55 McCrae Street, Fort Edward, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates generally to the production of electrically conductive elements and more particularly to the production of electrically conductive elements whose resistance is substantially unaffected by changes in the ambient atmosphere.

Basically, these conductive elements comprise an insulating base sheet having a conductive coating or film consisting of a conductive material dispersed throughout a non-conductive colloidal silica binder. The nature of the materials and concentrations used determine the electric conductivity of the resulting coatings. To this coating are applied spaced electrodes and when electricity is passed through the conductive coating via these electrodes, heat is produced. The distance between the electrodes and the resistance of the coating determines the amount of heat developed per unit of surface area for a given voltage applied to the electrodes.

The colloidal silica used as a non-conductive, adhesive bonding agent or carrier for the conductive particles in the composition of the present invention is a unique colloidal dispersion. Such a colloidal silica is marketed under the trade mark "Ludox" by E. I. duPont de Nemours and Company and under the trade mark "Syton" by Monsanto Chemical Company. For example, the "Ludox" colloidal silica generally marketed is composed of 29 to 31%  $\text{SiO}_2$ , 0.29 to 0.39%  $\text{Na}_2\text{O}$  and a maximum of 0.15% sulfates as  $\text{Na}_2\text{SO}_4$ , and is obtainable in the form of a

water slurry containing about 30% solids. The silica particles are extremely small, ranging from about 0.01 to 0.03 microns in maximum dimension. The colloidal dispersion has an insolubilizing action on water soluble substances, such as water soluble synthetic resins. Another very important property of such a colloidal silica is that the silica is irreversibly precipitated. Once the colloidal silica is dispersed, in water for example, and dried, it becomes irreversible and cannot be redispersed.

Ludox colloidal silica and the method of making it is described in detail in Bird's United States Patent No. 2,244,325 dated June 3, 1941; Bechtold and Snyder's United States Patent No. 2,574,902 dated November 13, 1951, and Iler's United States Patent No. 2,597,872 dated May 27, 1952. These patents further describe Ludox colloidal silica as a stable aqueous silica sol generally having a silica-alkali ratio from about 60:1 to 130:1 containing discrete silica particles, having a molecular weight, as determined by light scattering of more than one-half million. It has a relative viscosity, at 10 percent  $\text{SiO}_2$ , from 1.15 to 1.55 and generally contains from 20 to 35 per cent by weight of  $\text{SiO}_2$ . The silica-alkali ratio of Ludox silica is calculated at  $\text{Na}_2\text{O}$  and may be as low as 10:1 but it is advantageous to use a Ludox silica containing a silica-alkali ratio of between about 60:1 to 130:1. The silica-alkali ratio makes it obvious that the silica and alkali are combined in a special manner not found in conventional metal alkali silicates since the latter cannot be prepared in a form soluble and stable in aqueous solutions at ratios above 4:1. The alkali present is not uniformly distributed throughout the  $\text{SiO}_2$  particles as it is in conventional silicate such as water glass but is substantially all outside the  $\text{SiO}_2$  particles. The alkali is present as a stabilizer for the  $\text{SiO}_2$  sol and prevents condensation of the

[Price 4s. 6d.]

Price 33p

SiO<sub>2</sub> particles. Other stable colloidal silica sols can also be used such as discussed in Alexander and Iler's United States Patent No. 2,892,797 dated June 30, 1959 and marketed by duPont under the trade name Ludox A.M.

Ludox colloidal silicas are generally prepared by passing a silicate through an ion exchange resin to remove the alkali as described in Bird's United States Patent No. 2,244,235 dated June 3, 1941. If all of the alkali is removed from the silicate, the resulting sols are not stable, but they can be stabilized by adding a small amount of alkali such as Na<sub>2</sub>O or K<sub>2</sub>O.

It is also particularly advantageous to use "Ludox" silica having a particle size of less than 30 millimicrons (0.03 micron), although the particles of "Ludox" may be of colloidal dimensions, that is, particles having an average size not exceeding 100 millimicrons (0.1 micron) nor less than about 1 millimicron (0.001 micron). The particle size of Ludox colloidal silica is determined as the average size of particle present when the solution is diluted to about 0.1% SiO<sub>2</sub> with water and dried in a very thin layer deposit as described in the above-mentioned Bird's United States Patent No. 2,244,325.

It is also advantageous to use a Ludox silica containing between about 29-30% SiO<sub>2</sub> although higher and lower amounts can be used. Stable Ludox silica sols containing 5 to 15% SiO<sub>2</sub> can be prepared according to Bird's United States Patent No. 2,244,325 dated June 3, 1941, while the more advantageous Ludox silica sols containing 20 to 35% by weight SiO<sub>2</sub> can be prepared according to Bechtold and Snyder's United States Patent No. 2,574,902, dated November 13, 1951. For a further and more detailed description of Ludox colloidal silica and to the method of making it, the above patents may be referred to.

In preparing the coating the colloidal silica is mixed with electrically conductive particles of a much larger size than the silica particles and formed into a slurry. The conductive particles may range in size from about 1 to 10 microns. A typical example of a composition of the present invention in parts by weight is as follows:

Colloidal Silica "Ludox"	75 (30% solids)
Fine Graphite Powder	25

Water is used as a dispersing medium and it is only necessary to add sufficient water to form a coatable composition. The extremely active particles of the colloidal silica act as a very strong binder in themselves, and it is not necessary to use any soluble binder at all with the above composition.

The following composition has been found satisfactory in producing these elements and comprises an aqueous dispersion of particles of electrically conductive material such as

graphite and an alkali stabilized colloidal silica in the form of dispersed particles having a particle size of about 1 to 100 millimicrons and having substantially all the alkali outside the silica particles. This coating and variations thereof are more particularly described in British Patent No. 772,449.

In use, the elements may be saturated and encapsulated in plastics, bonded to various structures, for example, walls of a room, or merely cut into lengths and used as they are.

Generally, in producing electrically conductive elements, it has been the practice in the past to apply the composition containing electrically conductive material to an insulating base member such as Kraft paper, asbestos, Teflon (registered trade mark), by coating the base by any conventional procedure for coating paper or by spraying the conductive composition thereon. The Kraft paper was usually provided with a moisture resistant resin layer to prevent wrinkling of the paper during the coating operation.

With electrically conductive elements produced with the above coating, problems arose with respect to resistance of the element within specified ranges. Specifically, unpredictable and permanent changes in the resistance of these elements would result after their production. The exact reason for these changes in resistance are not known, but it is believed that the changes in the moisture content of the coating composition of the elements is important. Nevertheless, these changes being permanent and unpredictable in nature, made it difficult to determine, during the production run, what the final resistance of the elements would be after they were produced and shipped to the consumer.

To avoid these permanent changes in resistance, the procedure previously used in producing the conductive coatings included the step of drying the coating after it was applied to the insulating base. These coated insulated bases could then be stored in this manner without producing any significant change in their resistance. One reason for this is the fact that even though the paper and the coating were wet at one time, they were not wet for a sufficiently long period of time to affect the resistance desired.

Sometimes it has been desirable to secure a top insulating material over the electrodes and coating, but when these electrodes and top insulating layer are applied to the conductive coating by an aqueous technique, the coating again becomes wet. If the wet coating is allowed to stand for any period of time, the resistance changes, and this change is permanent. Therefore, if we start out to manufacture a coating having an initial resistance of, for example 60 ohms, one can never be sure what the resistance of the end product will be. Generally with low resistance elements, the resistance tolerances of the final

70

75

80

85

90

95

100

105

110

115

120

125

130

product is plus or minus 10%. If the resistance changes during wet storage or during the application of the electrodes and insulating material to, say, 75 ohms, the entire production run will not be within specification and it will have to be discarded or used in some other manner than originally intended.

It is, of course, possible to dry the coating immediately after the combining step of the electrode and top insulating layer as was done after the coating was first applied. However, this adds unnecessary expense to the production procedure and ultimately increases the cost of the end product. It, of course, would be advantageous to eliminate this drying step and to have a conductive coating which would not change in resistance during storage when wet or after it is combined with electrodes and the top insulating material.

The change in resistance of the conductive coating is especially apparent where the electrodes and the top insulating layer are adhered to the conductive coating by means of an adhesive containing alkali such as sodium silicate or water glass. When such an adhesive is used however, it is very advantageous to store the combined element while wet to give the alkaline adhesive sufficient time to penetrate the various components of the end structure in order to impart thereto adequate strength. If such combined structure is immediately dried, the adherence of the electrodes and the top insulating layer to the conductive layer is very weak and because of this weak adherence many uses to which the element could be put are eliminated. As previously stated, the storing of these elements while wet results in a permanent change in the resistance of the elements prohibiting any prior determination of the final resistance which would be obtained from the product.

One reason why the resistance change is even more pronounced when using an alkaline adhesive such as sodium silicate than when such an adhesive is not used is probably due to the presence of the additional alkali placed adjacent to or in the porous coating.

The resistance of the elements will be higher when they are wet than when they are dry. For example, an electrically conductive coating having a resistance of 60 ohms per square when dry might have a resistance of 90 ohms per square when wet. Prior to this invention, if the resistance of a coating were to rise from 60 ohms per square to 90 ohms per square during the wet combining step and the coating was allowed to stay in a wet condition for any length of time, the resistance might tend to stabilize itself around approximately 90 ohms per square when subsequently dried. On the other hand, the wetting operation might increase the resistance to a considerably higher value than 90 ohms per square; or upon drying, the resistance value might even go down rather than become stabilized at the

higher value. It can thus be seen that the effect that wetting has on the resistance of the coating is quite unpredictable.

Under this procedure used in the past, disadvantages also resulted even if the coating was dried immediately after becoming wet during its production. These disadvantages occurred in actual use. For example, if the final product after being installed in a wall of a room, was allowed to become wet for any length of time, the resistance of the element would increase and become stabilized at this high value.

According to the teaching of the present invention, a final element can be produced with a coating having a predetermined resistance which is the same as the initial resistance of the coating composition before it is applied to the insulating base. This is possible even though the coating is wetted during the combining steps and stored in a wet condition for considerable periods of time. Although the resistance of the coating may increase from 60 ohms per square to 90 ohms per square, for example, when it is wetted, it will not become stabilized at 90 ohms per square but will return to its original resistance value when it is finally dried.

This result is obtained by heating the coating as described herein to a certain critical temperature for a sufficient period of time to stabilize the conductive coating. It is not known exactly why this heating stabilizes the coating, but it is believed that one of the reasons is that the water contained in the hydrated silica of the coating is condensed out and that the coating is then able to resist any moisture or alkali attack from both the materials in the coating composition and the materials in the water based adhesive that might be used in uniting the various components of the element.

The temperatures to which the conductive coatings described above must be heated in order to effect this stabilization is at least 312° F. Much higher temperatures can, of course, be used; but any lower temperature will not produce the results desired. If, for example, the coating is heated to 305° F, the subsequent change in the resistance of the element may be more pronounced than if the coating were heated to 300° F. The maximum temperatures which can be used will depend mainly upon the components and materials used in the base supporting layer as well as in the coating composition itself. Certainly, if a material such as cellulose is used as a base for the conductive coating, the curing temperature should be below that which would cause injury to the base coating.

The exact temperature which might be most advantageous will also depend upon the coating equipment available and the speed at which the coated insulating base is passed through the dryer. The critical temperature

is not that of the dryer itself but the temperature obtained by the coating. Generally, the conductive coatings can be stabilized against resistance change as discussed herein by heating the coating composition to a temperature of 312° F. in a matter of a few seconds so long as the coating itself reaches this critical temperature.

It is understood that with variations in the coating, different stabilization temperature will result and that the specific stabilization temperature for any coating may be determined by experiment.

In actual practice, the insulating base is coated with an aqueous suspension of conductive particles and colloidal silica. This wet coated insulated base is then transferred to the dryer which may, for example, be heated to 350° F. Before the coating can reach the stabilizing temperature it must be dried and the water removed. Thus, during the first period that the wet coated paper is in the dryer, a drying function is being performed and it is not until the paper is nearing the end of the dryer that it actually reaches the stabilizing temperatures. The wet coating can, of course, be dried at any temperature so long as the coating itself reaches the stabilizing temperature for a short period of time on the order of 15 to 20 seconds.

Thus the actual time that the conductive coating and insulating base are in the dryer will include that necessary for drying the coating as well as that necessary for stabilizing the coating.

In one coating operation the temperature of the dryer was maintained at about 315° F. and a 6 inch width web coated with the conductive coating described herein was passed through a 16 foot dryer at about 8 feet per minute. The conductive coating on the paper at the exit end of the dryer had a measured temperature of 315° F. and this was sufficient to stabilize the coating. In larger coating operations, for example, 46 inch width, the wet paper was transferred through the dryer at approximately 100 feet per minute. In view of the speed of the paper passing through the dryer it was advantageous to extend the length of the dryer and to heat the dryer in this case to a temperature of 400° F. The conductive coatings leaving the dryer had a measured temperature of about 400° F.

After the drying operation, the resulting product may be shipped directly to the consumer. Alternatively, electrodes and a top layer of insulating material may be applied over the coating. The product being wet due to the combining steps may still be rolled up and stored without drying.

An example of one of the preferred methods used for producing heating elements according to the teaching of the present invention is as follows:

50 pounds of an aqueous alkaline stabi-

lized colloidal silica having 31% solids and marketed by the E. I. duPont Company under the trademark "Ludox" HS was thoroughly mixed with 100 lbs. of graphite Acheson Grade 38. To this pre-mix, 300 pounds of the same Ludox HS was added and thoroughly mixed therewith to form a dispersion of coatable consistency. This coating composition was applied using a 4 mil wet gap metering roll to a web of asbestos paper having a suitable wet strength and a thickness of about 7 mils. The coating composition applied to the asbestos web was designed to give a coating resistance of 60 ohms per square.

The coated asbestos base was then passed through a dryer 16 feet in length at the rate of about 8 feet per minute. The temperature in the dryer at the last stage was measured at 350° F. and the temperature of the paper and conductive coating at the exit of the dryer was measured by a thermocouple at 350° F. The thickness of the resulting dried coating was about 1.7 mils and the resistance of the coating upon exit from the dryer was measured and found to be 60 ohms per square. Electrodes were applied to each end of the web along the length of the web and a top insulating asbestos layer was next applied over the conductive coating using a sodium silicate adhesive. The water present in the sodium silicate adhesive wet the coating and the resistance of the wet coating varied and measured anywhere from between 92 to 100 ohms per square. After the electrodes and top insulating layer were applied, the web was rolled up and stored in the wet condition. The conductive web was then allowed to dry by exposing it to air and the final resistance of the dry coating was measured and found to be 60 ohms per square, the original resistance intended. The coating at this stage can, of course, be dried in other manners if desired even by the use of positive drying means but in all instances, the resistance will return to approximately 60 ohms per square and will not be permanently affected.

As previously discussed, unless the element is heated to the temperature of at least 312° F., the conductive coating will permanently change in resistance upon exposure to moisture. The exposure to moisture can occur in other manners aside from contact with an adhesive containing moisture such as by exposure to weather and high humidity conditions.

It is understood that various changes could be made in the procedure set forth and in the compositions hereinabove described without departing from the scope of the present invention.

#### WHAT WE CLAIM IS:—

1. A method of producing an electrically conductive stable coating which comprises the

- steps of applying to an insulating base an electrically conductive composition comprising an aqueous dispersion of particles of electrically conductive material and a stabilized colloidal silica in the form of dispersed particles having substantially no alkali within the silica particles, and heating the electrically conductive coating to a temperature sufficient to stabilize said coating whereby its resistance is not permanently affected by subsequent variations in the moisture content thereof.
2. The method of producing an electrically stable conductive element, which comprises the steps of applying to an insulating base an electrically conductive composition comprising an aqueous dispersion of particles of electrically conductive material and a stabilized colloidal silica in the form of dispersed particles having substantially no alkali within the silica particles, heating the electrically conductive coating to a temperature of at least 312° F to effect stabilization of the coating, applying electrodes at spaced points on said coating, adhering a sheet of insulating material over said coating and electrodes with sodium silicate adhesive, and storing the resulting element in a wet condition at room temperature so as to allow the coating to dry.
3. An article of manufacture comprising an insulating base, and an electrically conductive composition adhered thereto to form a coating which has been heated to a temperature of at least 312° F to stabilize the same whereby its resistance is not permanently affected by subsequent variations in the moisture content of said coating, and which comprises particles of electrically conductive material distributed throughout and bonded together with colloidal silica particles having substantially no alkali combined within the silica particles.
4. An article of manufacture comprising an insulating base, an electrically conductive composition adhered to said base to form a coating which has been heated to a temperature of at least 312° F to stabilize the same whereby its resistance is not permanently affected by subsequent variations in its moisture content and which comprises particles of electrically conductive material distributed throughout and bonded together with colloidal silica particles having substantially no alkali combined within the silica particles, a pair of electrodes disposed on said electrically conductive coating at a predetermined spaced position with respect to each other, and a sheet of insulation material secured to said coating with sodium silicate and covering said electrodes.

CRUIKSHANK & FAIRWEATHER,

Chartered Patent Agents,  
29 Southampton Buildings,  
Chancery Lane,  
London, W.C.2.

and

29 St. Vincent Place, Glasgow,  
Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1966.

Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

